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Author's Review

Stereochemical Aspects of Sulfoxides and Metal Sulfoxide Complexes*

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Structural parameters of free and metal coordinated sulfoxides are reviewed and updated average values are derived. For uncoordinated sulfoxides, the average S–O bond distance is 1.4918(9) Å. This value is lengthened to 1.528(1) Å upon O-coordination to metal ions, while it is reduced to 1.4731(6) Å upon S-coordination. The sulfoxide bonding and bridging modes are discussed together with some stereochemical features.

Key words: sulfoxide, metal complexes, crystal structures, stereochemistry, average dimensions.

INTRODUCTION

Dimethyl sulfoxide (dmso) is a widely used aprotic solvent, characterized by a large dipole moment and high polarizability,[1] which enable it to interact with molecules and ions through dipolar interactions,[2] as well as to coordinate metal ions forming a great variety of stable metal complexes.[3,4] The structure of dmso is pyramidal around the sp^3 hybridized sulfur atom, as shown, in the solid state, by X-ray determinations,[3,4] and, in the gas phase, by microwave spectroscopy and electron diffraction studies.[5,6] The S–O bond is highly polarized, with positive and negative charges localized on S and O, respectively, as shown by experimental evidence,[3] and theoretical calculations.[7] This structure makes dmso act as an ambidentate ligand,

* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

which can interact through its oxygen (dmso-O) or sulfur (dmso-S) atom depending on the 'hardness' and 'softness'[8] of the binding atoms. A survey of known X-ray structures has shown that S-bonding is essentially limited to metal atoms of groups 8–10, in the second and third transition series, being particularly favoured for platinum.[4] Anyhow, electronic factors, due to the metal oxidation state and nature of the ancillary ligands, together with steric factors, can produce linkage isomerism. Very hard species, such as hydrogen and alkaline or alkaline-earth metal ions, always interact through the dmso oxygen atom. This property is very important for understanding the behaviour of dmso – protic/aprotic solvent solutions.[2,9] In this regard, it is of interest to mention the ability of dmso to stabilize biological membrane structures at low temperatures, preventing freezing damage to living tissues during low-temperature preservation. This is probably due to retardation of ice formation within the cells because of the H-bond formation with dmso.[10] Similarly, mixing of water with dmso causes a change in the intraprotein hydrogen bonds, explaining the protein denaturation process in this and other hydrophilic solvents.[11,12] Finally, the formation of metal ion-solvent complexes (*e.g.* Na^+-dmso) has a profound effect on the protein stability and activity in organic solvents.[13]

Anyhow, relevance of dmso in biochemical processes is not restricted to solvent effects. In fact, ruthenium-dmso complexes have been used as precursors to radiosensitizing agents,[14] and are widely investigated for their antitumour and, in particular, antimetastatic activity against several murine tumour models.[15] The complexes, soluble in water and able to diffuse through cell membranes for the presence of dmso, interact *in vitro* and *in vivo* with DNA, the N7 of the guanine bases appearing as the preferential site of attack.[16] The NMR structural investigation of the reaction product between d(GpG) and *trans*-$RuCl_2(dmso)_4$ has shown the formation of a stable compound characterized by a covalent bifunctional coordination of the bases to the metal centre.[17] In fact, the compound contains two *cis* N7 guanine moieties, in a head-to-head conformation, with two *cis* dmso-S ligands, each *trans* to a guanine base. A chloride ion and one water molecule complete the octahedral coordination of the metal atom.[17] On the other hand, it is possible that the antimetastatic action of the ruthenium-dmso complexes does not derive from a direct interaction with DNA of cancer cells, but from their interaction with extracellular components yielding a reduced capacity of tumour cells to escape from the primary tumour and migrate to other organs.[18] These interactions could involve a hydrogen bonding scheme in which the dmso oxygen atoms would act as acceptor centres. In fact, it is well known that even in metal complexes the S–O bond is polarized, with a significant negative charge localized on the oxygen atoms.[3,19,20]

The basic features of the interaction of dmso with protic ligands have been studied on simple models using quantum chemical calculations,[2,7,9] while the structures of the solvation shells around Na^+ in liquid dmso have been studied in terms of the ion-solvent radial and orientational distribution functions.[21] The conformational properties of ruthenium-dmso complexes containing nitrogen bases have been studied by means of NMR techniques,[22–26] generally associated with X-ray,[22,24–26] and molecular mechanics (MM) studies.[24–27] The scope of this paper is that of providing a survey of the experimental evidence of the influence of H-bonding and metal ion interactions on the structural parameters of free sulfoxides. Particular attention is also paid to the bonding and conformational properties of the sulfoxide ligands.

RESULTS AND DISCUSSION

Free and H-bonded Sulfoxides

Recently, a statistical analysis of sulfoxide crystal data has shown that the best estimate of the S–O bond length in free dmso is provided by the average value from solvate crystal structures, rather than from pure dmso crystal structures, because of the inaccuracy of the latter.[4] Averaging the data from the 7 (n) most accurate crystal structures, the 'semi-weighted mean' value ($<x_s>$) of 1.495(4) Å was obtained with a standard deviation (σ) of 0.010 Å.[4] A similar value was obtained from other free sulfoxides of the type R'R''SO, with a great variety of R' and R'' groups: $<x_s>$ = 1.492(1) Å, n = 33, σ = 0.008 Å.[4] Averaging all the available data (n = 40), a mean value of 1.492(1) Å was obtained with σ = 0.009 Å. The small value of the standard deviation suggests that the S–O bond distance is not dramatically affected by the nature of the sulfinyl substituents, at least within the limits of accuracy of the available structure determinations. Interestingly, values of 1.487(5) and 1.49(1) Å have been found also in two cyclic sulfoxides.[4] Furthermore, it is worth noting that values about 1.483(3)–1.485(6) Å have been found in the gas phase,[6] and that a value of 1.487 Å has been assumed as the 'unstrained' value of the S–O bond distance in recent Allinger's MM3 force field for sulfoxides.[28] According to this force field, the optimized S–O bond distances are 1.488, 1.489 and 1.496 Å for dimethyl, methylethyl and diisopropyl sulfoxides, respectively.

Larger values [1.499(5)–1.529(8) Å] were found only when the sulfoxide oxygen atoms appeared to be involved in hydrogen-bonding.[4] This effect is in agreement with the definitely long distances found in the bis-sulfoxide

TABLE I

Bond lengths /Å and angles /° for uncoordinated not cyclic sulfoxides R'R''SO

R'	R''		S–O	S–C(R')	S–C(R'')	C–S–C	O–S–C(R')	O–S–C(R'')	Ref.
CH_3	CH_3	a	1.48(2)	1.84(2)	1.81(3)	101(1)	104.7(8)	102.0(8)	31
			1.493(4)	1.794(7)	1.768(8)	97.8(5)	107.3(3)	101.0(3)	
CH_3	CH_3	a	1.50(1)	1.68(3)	1.68(2)	98(1)	109(1)	111(1)	32
			1.50(1)	1.74(2)	1.79(2)	98(1)	106.9(9)	105.8(9)	
CH_3	CH_3	a, b	*1.504(2)*	1.772(4)	1.770(3)	97.7(2)	106.5(2)	106.5(1)	33
CH_3	CH_3	a, c	*1.509(1)*	1.782(2)	1.800(2)	98.3(1)	104.65(9)	104.82(9)	34
CH_3	CH_3	d	*1.530(8)*	1.75(1)	1.76(1)	100.3(6)	103.0(5)	105.1(5)	35
			1.561(7)	1.74(1)	1.75(1)	99.4(5)	101.2(5)	104.5(5)	
$C_7H_8NO_2S$	CH_3		1.482(2)	1.837(3)	1.794(3)	96.5(1)	104.1(1)	104.7(1)	36
$C_{10}H_9N_2O_2S$	CH_3		1.484(3)	1.790(3)	1.782(3)	95.9(2)	104.3(2)	106.4(2)	37
			1.479(3)	1.788(3)	1.796(6)	95.8(2)	104.6(2)	104.6(3)	
$C_{10}H_9N_2O_3S$	CH_3		1.468(3)	1.795(3)	1.781(4)	96.6(2)	107.8(1)	105.9(2)	35
$C_5H_7O_2S$	C_6H_5		1.478(5)	1.819(7)	1.799(7)	98.4(3)	106.2(3)	106.9(3)	38
$C_{14}H_{12}O_2S_2$	C_6H_5		1.475(3)	1.798(3)	1.798(4)	98.2(2)	106.8(2)	106.4(2)	39
$C_{14}H_{12}O_3S_2$	C_6H_5		1.494(3)	1.811(3)	1.794(4)	92.6(2)	104.4(2)	108.1(2)	39
$C_{14}H_{12}CrNO_6$	C_6H_5		1.48(1)	1.72(1)			107.3(7)		40
$C_{10}H_{10}NO$	C_8H_{17}	e	1.50(1)	1.79(1)	1.79(1)	99.3(5)	105.6(6)	107.7(5)	41
			1.50(1)	1.78(1)	1.79(1)	97.0(5)	106.5(7)	108.0(6)	
$C_{10}H_{10}NO$	C_8H_{17}	f	1.495(4)	1.798(6)	1.792(6)	98.3(3)	105.9(3)	107.5(3)	41
$C_{10}H_{10}NO$	C_5H_5O		1.488(6)	1.813(7)	1.787(5)	98.2(3)	106.4(3)	107.0(3)	41
$C_9H_{11}O_4$	$C_{10}H_{17}O$	g, h	*1.510(9)*	1.78(1)	1.802(8)	99.0(4)	108.2(5)	105.5(4)	42
$C_{13}H_{12}O_2S_2$	$C_{10}H_{16}O$	g, i	*1.509(9)*	1.83(1)	1.86(1)	96.3(5)	105.1(5)	104.7(5)	43

[a] Solvate. [b] H-bonding with 1,4,5,8-naphtalenetetracarboxylic acid (O···O, 2.598(2) Å). [c] H-bonding with *N,N'*-ditosyl-*p*-phenylenediamine (O···N, 2.789(2) Å). [d] In $[(dmso)_2H]^+$ (O···O, 2.43(1) Å) of $[(dmso)_2H][OsCl_4(NO)(dmso\text{-}O)]$. [e] (*S*) sulfinyl diastereomer, two crystallographically independent molecules. [f] (*R*) sulfinyl diastereomer. [g] Intramolecular H-bond between the sulfinyl O atom and the OH group of R''. [h] (O···O, 2.71(1) Å). [i] (O···O, 2.74(1) Å).

TABLE II

Bond lengths /Å and angles /° for uncoordinated cyclic monosulfoxides

Ring size	Ring atoms		S–O	S–C'	S–C''	C'–S–C''	O–S–C'	O–S–C''	Ref.
5	S–C'–N–N–C''		1.484(2)	1.848(3)	1.824(3)	85.4(1)	109.3(1)	104.5(1)	37
5	S–C'–C–C–C''		1.484(3)	1.781(2)	1.781(2)	91.3(2)	112.7(1)	112.7(1)	44
5	S–C'–C–C–C''	[a]	*1.512(5)*	1.786(5)	1.815(6)	91.2(3)	106.4(4)	106.4(3)	45
5	S–C'–C–C–C''	[b]	*1.53(2)*	1.79(3)	1.82(3)	93(1)	106(1)	106(1)	46
6	S–C'–C–C–S–C''		1.497(3)	1.807(4)	1.834(4)	96.9(2)	106.6(2)	104.3(2)	47
6	S–C'–C–C–S–C''		1.508(2)	1.805(3)	1.828(2)	97.1(1)	106.8(1)	105.3(1)	48
6	S–C'–C–C–S–C''	[c]	1.497(1)	1.830(2)	1.806(2)	98.2(2)	105.2(1)	105.4(1)	49
6	S–C'–C–C–S–C''	[d]	1.484(2)	1.843(2)	1.812(3)	99.2(2)	108.4(2)	106.9(2)	49
8	S–C'–C–C–S–C–C–C''		1.43(3) [e]	1.798(3)	1.786(3)	103.6(1)	107.4(6)	108(5) [e]	50

[a] Intramolecular H-bond between the sulfoxide O atom and the OH group of a hydroxyethylthio group (O···O, 2.672(7) Å).

[b] Intermolecular H-bonding with the two O atoms of a *neo*-inositol group (O···O, 2.65, 2.69 Å).

[c] *trans* isomer. [d] *cis* isomer. [e] Average value for two S–O positions.

TABLE III

Bond lengths /Å and angles /° for uncoordinated not cyclic disulfoxides RS(O)R'S(O)R

R	R'		S–O	S–C(R)	S–C(R')	C–S–C	O–S–C(R)	O–S–C(R')	Ref.
C_6H_5	C_2H_4	[a]	1.491(4)	1.792(4)	1.813(4)	98.5(1)	106.7(1)	106.4(1)	51
		[b]	1.496(7)	1.800(7)	1.808(7)	98.5(2)	107.4(2)	106.3(2)	51
			1.488(7)	1.790(7)	1.803(7)	98.0(2)	107.4(2)	105.8(2)	
C_9H_{20}	C_2H_4	[a]	1.460(4)	1.798(3)	1.820(3)	98.1(1)	113.3(2)	105.5(2)	52
C_7H_7	C_6H_4		1.481(4)	1.805(4)	1.821(6)	96.6(2)	106.3(2)	105.5(2)	53
CH_3	$C_{15}H_{14}$		1.490(3)	1.802(3)	1.858(3)	103.5(1)	104.4(1)	107.6(1)	54
			1.496(2)	1.785(3)	1.856(3)	101.4(1)	106.3(2)	105.1(1)	
C_6H_5	C_6H_8	[b]	1.487(4)	1.791(5)	1.840(5)	96.8(2)	106.1(2)	107.5(2)	55
			1.508(4)	1.802(5)	1.817(5)	100.2(2)	107.0(2)	108.3(2)	
C_6H_5	$C_8H_6O_3S$		1.486(3)	1.803(3)	1.824(4)	92.2(1)	106.8(2)	101.2(2)	39
			1.481(3)	1.789(3)	1.858(3)	96.2(2)	108.3(2)	105.8(2)	

[a] *meso* form. [b] *rac* form.

TABLE IV

Bond lengths /Å and angles /° for uncoordinated mono-cyclic disulfoxides –RS(O)R'S(O)–

Ring size	R	R'		S–O	S–C(R')	S–C(R'')	C–S–C	O–S–C(R')	O–S–C(R'')	Ref.
6	$CH_2(CHMe)_2$	CH_2		1.491(5)	1.821(6)	1.819(5)	96.4(2)	104.9(2)	107.4(2)	48
				1.509(4)	1.812(5)	1.821(5)	96.7(2)	105.6(2)	106.8(2)	
	C_6H_4	C_6H_4		1.48(2)	1.83(2)	1.75(2)	96.8(1)	103.2(1)	108.2(1)	56
				1.47(2)	1.72(2)	1.87(2)	95.7(1)	106.3(1)	109.7(1)	
	C_6H_4	C_6H_4	[a]	1.483(7)	1.78(1)	1.786(9)	96.5(4)	105.5(4)	105.9(4)	57
				1.471(7)	1.793(9)	1.782(9)	95.2(4)	108.4(4)	108.1(4)	

TABLE IV (continued)

	C_2H_4	C_2H_4	b, c	*1.51(2)*	1.74(2)	1.84(2)	98(1)	109(1)	107(1)	58
			b, d	*1.56(2)*	1.76(2)	1.73(2)	103(1)	103(1)	105(1)	
	C_2H_4	C_2H_4		1.50(1)	1.80(1)	1.80(1)	98.5(5)	107.4(5)	105.9(5)	59
				1.49(1)	1.79(1)	1.79(1)	96.1(5)	107.6(5)	106.8(5)	
				1.50(1)	1.83(1)	1.79(1)	97.8(5)	107.6(5)	105.7(5)	
			e	*1.51(1)*	1.77(1)	1.83(1)	97.6(5)	104.9(5)	106.8(5)	
	CPh_2	C_3H_6		1.489(6)	1.889(7)	1.799(7)	100.5(6)	110.0(5)	105.2(5)	60
				1.493(6)	1.902(7)	1.814(7)	99.4(6)	109.5(5)	105.3(5)	
	CHEt	C_3H_6		1.493(2)	1.792(2)	1.798(3)	97.5(1)	106.4(1)	106.9(1)	61
				1.496(2)	1.783(2)	1.800(3)	96.9(1)	106.4(1)	107.0(1)	
	CH_2	C_3H_6	f	1.487(5)	1.80(1)	1.82(1)	98.4(4)	108.4(4)	106.2(4)	62
				1.509(7)	1.81(1)	1.817(9)	97.9(4)	109.0(4)	107.3(4)	
	CH_2	C_3H_6	g	1.498(4)	1.799(7)	1.804(6)	96.1(3)	104.4(2)	107.0(2)	62
				1.511(4)	1.794(6)	1.794(6)	97.4(3)	106.5(2)	106.2(3)	
	CHPh	C_3H_6		1.465(3)	1.834(5)	1.803(5)	96.9(2)	104.1(2)	106.7(2)	49
				1.498(3)	1.833(4)	1.787(5)	97.0(2)	104.5(3)	107.0(3)	
	CH(OH)Ph	C_3H_6		1.509(5)	1.830(8)	1.816(8)	96.4(8)	105.1(6)	105.4(6)	63
			h	*1.524(5)*	1.817(8)	1.800(8)	98.7(8)	104.3(6)	103.0(6)	
8	$C_{10}H_6$	C_3H_6		1.487(6)	1.816(7)	1.805(7)	99.5(3)	106.3(3)	103.7(3)	50
				1.496(5)	1.808(6)	1.813(7)	98.2(3)	107.3(3)	105.1(3)	
	C_3H_6	C_3H_6		1.513(6)	1.823(7)	1.816(7)	101.8(6)	103.1(5)	106.3(5)	65
				1.504(6)	1.809(7)	1.825(7)	100.0(6)	105.4(5)	106.6(5)	
	C_3H_6	C_3H_6		1.498(4)	1.815(5)	1.803(6)	100.9(3)	105.9(2)	103.7(2)	66
				1.502(4)	1.803(5)	1.806(6)	102.8(2)	105.2(3)	107.0(2)	

[a] Refined values. [b] H-bonding with Ho-coordinated water molecules. [c] (O···O, 2.64 Å). [d] (O···O, 2.71, 2.81 Å). [e] H-bonding with one Nd-coordinated water molecule (O···O, 2.62 Å). [f] *cis* isomer. [g] *trans* isomer. [h] Intermolecular H-bond with the OH group of R (O···O, 2.69 Å).

TABLE V

Bond lengths /Å and angles /° for uncoordinated fused ring cyclic sulfoxides

Ring size	Ring atoms		S–O	S–C'	S–C''	C–S–C	O–S–C'	O–S–C''	Ref.
5, 5	S–C'–C–C–C''		1.502(4)	1.810(4)	1.837(4)	91.7(2)	108.0(2)	106.3(2)	67
			1.503(5)	1.824(4)	1.825(4)	92.2(2)	107.8(2)	106.5(2)	
5, 5	S–C'–C–C–C''	a	*1.518(6)*	1.812(5)	1.795(6)	87.7(2)	107.7(3)	107.4(3)	67
			1.515(5)	1.791(5)	1.799(6)	88.6(3)	107.6(3)	107.0(3)	
5, 5	S–C'–C–C–C''	b	1.495(5)	1.807(6)	1.845(5)	89.7(2)	104.5(2)	106.7(2)	68
			1.505(5)	1.816(5)	1.844(5)	89.2(2)	106.2(3)	107.8(2)	

[a] H-bonding with water molecules (O···O, 2.83(1) and 2.91(1) Å).
[b] Two crystallographically independent molecules (A, B); possible weak intermolecular H-bonding in B (O···C, 3.045(7) Å).

hydrogen cations, $[(\text{sulfoxide-O})_2\text{H}]^+$, [1.528(4)–1.559(2) Å] and the still longer ones found in the protonated dimethyl and tetramethylene sulfoxides, $[(\text{dmso})\text{H}^+]$ (1.585(8) Å) and $[(\text{tmso})\text{H}]^+$ (1.589(3) Å).[4] The S–O bond length increases with increasing the O···H interaction. This trend in the S–O bond lengths is consistent with the decreasing of the S–O stretching frequency from free to H-bonded dmso (58 cm^{-1} in the dmso-H_2O adduct)[9] and to protonated sulfoxides (125 cm^{-1} and 188 cm^{-1} for $[(\text{dmso})\text{H}]^+$ and $[(\text{tmso})\text{H}]^+$, respectively),[4] showing a significant weakening of the S–O bonds. This trend is also confirmed by MO *ab initio* calculations.[9,29] In particular, a full geometry optimization of $[(\text{dmso})\text{H}]^+$, on a 3–21G(1d) basis, shows an increase of the S–O bond length from 1.490 Å, in dmso, to 1.599 Å, with a reduction of the ν(S–O) stretching frequency of 245 cm^{-1}.[29] All these data prove that in 'free' sulfoxides the S–O bond distance is expected to be about 1.49 Å, roughly in the range 1.48–1.50 Å, and not about 1.5–1.6 Å, as recently reported,[30] if room temperature values, not corrected for thermal motion, are considered.

In order to confirm that in free sulfoxides the S–O bond length is only slightly affected by the nature of the side groups, and the lengthening effect of H-bonding, Tables I–V list data for uncoordinated not cyclic and cyclic sulfoxides not reported in previous reviews.[31–68] Updated average values for the structural parameters of not cyclic and cyclic free sulfoxides are given in Tables VI and VII, respectively. These were calculated, as previously described,[4] merging the present work data with those already reported.[4] Statistic parameters show that the S–O and S–C bond lengths display a nearly symmetrical normal distribution, the mean values being very close to the medians and the lower and upper quartiles (q_l, q_u) being approximately symmetric about the medians. Angles generally show less symmetrical distributions. For most parameters, more than 94% of the observations lie

within ±2σ. With the exclusion of one value in the O–S–C angles of Table VI, no outliers (difference from the mean value greater than 4σ) are present.

From Tables VI and VII it can be seen that these data are in perfect agreement with previous values,[4] and that the S–O bond distances, excluding the values of H-bonded species (shown in italics in Tables I–V), average 1.492(1) Å, with a σ value of 0.010 Å, in spite of the quite different nature of the sulfinyl side groups, including cyclic ligands. As a matter of fact, the difference between not cyclic [1.490(1) Å] and cyclic [1.495(2) Å] sulfoxides seems statistically hardly significant. On the contrary, the S–C bond distances appear to be slightly longer in cyclic sulfoxides [1.812(2) Å *vs.* 1.796(2) Å]. On the other hand, angles can vary more significantly. For example, in the not cyclic sulfoxide 1,4-dimesityl-1,4-dithiabutane-1,4-dioxide, the O–S–C angles can be as large as 113.3(2)° (Table III) *vs.* the average value of 105.9(1)°, due to a partially eclipsed conformation,[52] while in the cyclic thiophene S-oxide the O–S–C angles of 112.7(1)° [44] (Table II) are again significantly wider than in other five-membered cyclic sulfoxides [*av.* 107.2(4)°]. In this last case, this is probably due to the aromaticity of the five-membered ring, which causes a greater repulsion between the S–O double bond and

TABLE VI

Average bond lengths /Å and angles /° for uncoordinated not cyclic sulfoxides

	S–O	S–C	C–S–C	O–S–C	S–O[a]
min.	1.460	1.720	92.2	101.0	1.460
max.	1.513	1.858	103.5	113.3	1.513
n	66	154	85	171	101
σ	0.010	0.025	1.6	1.6	0.010
median	1.492	1.796	98.0	106.0	1.493
q_l	1.485	1.782	97.0	104.9	1.486
q_u	1.497	1.810	98.5	106.9	1.499
% (±2σ)	95.5	94.2	94.1	95.9[b]	94.1
$\langle x \rangle_s$	1.490	1.796	97.8	105.9	1.4918
$\sigma(\langle x \rangle_s)$	0.001	0.002	0.2	0.1	0.0009
$\langle x \rangle_u$	1.491	1.795	97.8	106.0	1.492
$\sigma(\langle x \rangle_u)$	0.001	0.002	0.2	0.1	0.001
$\langle x \rangle_w$	1.4903	1.8034	97.65	105.76	1.4914
$\sigma(\langle x \rangle_w)$	0.0004	0.0004	0.02	0.02	0.0004

[a] Data including cyclic sulfoxides. [b] One outlier.

TABLE VII

Average bond lengths /Å and angles /° for uncoordinated cyclic sulfoxides

	S–O	S–C	C–S–C[a]	C–S–C[b]	C–S–C[c]	O–S–C[a]	O–S–C[b]	O–S–C[c]
min.	1.465	1.770	85.4	95.2	98.2	104.0	103.0	103.1
max.	1.513	1.879	93.0	103.0	103.6	112.7	110.0	107.4
n	35	83	14	28	7	28	56	13
σ	0.011	0.023	2.3	1.6	1.9	2.0	1.6	1.4
median	1.496	1.810	91.2	97.3	100.9	106.4	106.5	105.9
q_l	1.488	1.799	88.6	96.6	99.8	106.0	105.3	105.1
q_u	1.503	1.823	91.7	98.3	103.2	107.8	107.4	106.6
% ($\pm 2\sigma$)	94.3	96.4	92.9	96.4	100.0	92.9	92.9	100.0
$\langle x \rangle_s$	1.495	1.812	90.3	97.5	101.0	107.2	106.4	105.6
$\sigma(\langle x \rangle_s)$	0.002	0.002	0.6	0.3	0.7	0.4	0.2	0.4
$\langle x \rangle_u$	1.495	1.812	90.3	97.6	101.0	107.0	106.4	105.6
$\sigma(\langle x \rangle_u)$	0.002	0.003	0.6	0.3	0.7	0.4	0.2	0.4
$\langle x \rangle_w$	1.4947	1.8102	88.69	96.98	102.6	108.51	106.36	105.5
$\sigma(\langle x \rangle_w)$	0.0007	0.0006	0.08	0.05	0.1	0.05	0.03	0.1

[a] Five-membered rings.[b] Six-membered rings.[c] Eight-membered rings.

the S–C bond pairs. In any case, as a general rule, the C–S–C bond angles increase from five- to six- and eight-membered rings [90.3(6)°, 97.5(3)° and 101.0(7)°, respectively], while the O–S–C angles slightly decrease [107.2(4)°, 106.4(2)° and 105.6(4)°, respectively]. The marked variation of the C–S–C bond angle in cyclic sulfoxides is obviuosly due to ring closure conditions, and, in fact, in the less strained six-membered rings it is very close to that of not cyclic sulfoxides [97.8(2)°].

Finally, it is evident from the present and previous data that the S–O bond distance is significantly lengthened upon H-bonding [range, 1.503(1)–1.529(8) Å], the lengthening depending on the nature of the donor ligand. Markedly longer distances are found in the protonated species, like $[(dmso)_2H]^+$ [range, 1.531(4)–1.561(7) Å] and $[(tmso)H]^+$ [1.589(3) Å],[4] which, actually, can be considered as 'coordination' compounds of H^+.

In this connection it seems of interest that in 1:1 adducts of phenyl iodonium bis(perfluoroalkanesulfonyl)methides with dmso, the latter interacts *via* O with the iodine atoms with a mean I···O distance of 2.58(2) Å, a distance that is significantly longer than the sum of the covalent radii (2.06 Å), but much shorter than the van der Waals distance (3.55 Å).[31] The mean sulfoxide S–O distance of 1.49(1) Å corresponds to that of an unperturbed

dmso, suggesting that the lack of a net covalent bond or of a strong electrostatic interaction has scarce influence on the S–O bond. However, it has been suggested that these I-dmso interactions affect the S–C bonds of the sulfonyl methide group.[31]

Metal Sulfoxide Complexes

Metal complexes whose structures were not included in the previous review[4] are given below, separated per groups.

Group 1: [Na($OC_6H_3Bu^t$-2,6)(μ-dmso-O)(dmso-O)]$_2$.[69]

Group 3: [Y(acetylacetonato)$_3$(dmso-O)(H_2O)] · dmso;[70] [Ln(picrate)$_3$(tdtd-O)$_{1.5}$], with tdtd = *trans*-1,4-dithiane-1,4-dioxide, and Ln = Ce, Eu [71] and Ln = Nd, Er;[72] [Ln(H_2O)$_3$(SO_3CF_3)(tdtd-O)$_2$](An), with Ln = Ho, An = ReO4 [58] and Ln = Nd, An = CF_3SO_3;[59] [(UO_2)(*p*-methylphenyl butyl sulfoxide-S)$_2$-(NO_3)$_2$].[73]

Group 4: [Ti_4O_6(dmso-O)$_{15}$]Cl_5 · 5dmso · 1/2H_2O, [TiO(dmso-O)$_5$]Cl_2;[32] [ZrF_4(dmso-O)$_2$]$_2$ (third structure determination[4]).[74]

Group 6: [CrCl(en)$_2$(dmso-O)]($ZnCl_4$), [CrCl(en)$_2$(dmso-O)][(NO_3)(ClO_4)], [CrCl(tn)$_2$(dmso-O)]($ZnCl_4$), [CrCl(dien)(dmso-O)$_2$]($ZnCl_4$), with en = ethylenediamine, tn = propylenediamine and dien = ethylenetriamine;[75] [$Cr(CO)_4$-(carb-S)], with carb = C(NC_4H_8)(C_4H_4O)S(O)(C_6H_5).[40]

Group 7: [(CuL)$_2$Mn(dmso-O)$_2$], with L = *N*-(4-methyl-6-oxo-3-azahept-4-enyl) oxamato.[76]

Group 8: (NH_3OH)[*fac*-$RuCl_3$(dmso-S)$_3$], ($MeNH_2OH$)[*fac*-$RuCl_3$(dmso-S)$_3$] and (Et_2NHOH)[*fac*-$RuCl_3$(dmso-S)$_3$];[77] [*fac*-$RuCl_3$(dmso-S)$_3$(N_2H_5)];[78] [Ru_3(dedtc)$_6$(dmso-S)$_2$](I_3)$_2$, with dedtc = *N*,*N*-diethyldithiocarbamate;[79] [Ru_2Cl_2(dmso-S)$_3$(μ-H)(μ-Cl)(μ-dmso-S,O)];[80] [$Ru_2Cl_4(CO)_2$(dmso-S)$_3$(μ-Cl)-(μ-dmso-S,O)];[81] [Ru_2Cl_4(dmso-S)$_5$] (second structure determination[4]);[82] [Ru_2Br_2(μ-Br)$_2$(diethylsulfoxide-O)$_2$($NO)_2$];[83] [*trans*-$OsCl_2$(dmso-S)$_4$];[84] [(dmso)$_2$H][*trans*-$OsCl_4$(NO)(dmso-O)].[35]

Group 9: [(C_5Me_4Et)Rh(tetramethylthiophene S-oxide)].[85]

Group 10: [{Ni(μ-acetato)[μ-bis(salicylidene)-1,3-propanediaminato]-(dmso-O)Ni}$_2$Ni];[86] [Pd(acetate)$_2$(dmso-S)],[87] [PtMe(1,10-phenanthroline-*N*,*N*')(dmso-S)](PF_6);[88] [*cis*-$PtBr_2$(dmso-S)$_2$] and [*trans*-PtI_2(dmso-S)$_2$];[89] [{*trans*-PtClMe(dmso-S)$_2$}($Sn_2OCl_2Me_4$)$_2$];[90] (NBu_4)[$PtCl_3$(dpso-S)], (NEt_4)-[$PtBr_3$(dpso-S)] and [*cis*-$PtCl_2$ (dpso-S)(*cyclo*-C_3H_5CN)], with dpso = diphenylsulfoxide;[91] [*cis*-$PtCl_2$(*rac*-bpsel-S,S')] with bpsel = 1,2-bis(phenylsulfinyl)-ethylene;[92] [*cis*-$PtCl_2$(*rac*-bprse-S,S')] with bprse = 1,2-bis(*n*-propylsulfinyl)ethane;[93] [*cis*-$PtCl_2$(PEt_3)]$_2$(μ-*meso*-bpse-S,S')], with bpse = 1,2-bis-(phenylsulfinyl)-ethane;[94] [*cis*-PtCl(dmso-S){Fe(C_5H_5)$C_5H_4C(CH_3)$=NOH}];[95] [*cis*-PtCl(dmso-S)-(OC_6H_4CH=NOH)] and [*mer*-$PtCl_3$(dmso-S){$Cl_2(O)C_6H_2CH$ =NOH}].[96]

Group 11: $[Cu(dmso\text{-}O)_4](ClO_4)_2$.[97]

Group 12: $[Hg(dmso\text{-}O)_6](CF_3SO_3)_2$.[98]

Group 13: $[AlS(dmso\text{-}O)(C_6H_2)Bu^t_3)]_2$.[99]

Group 14: $[(SnPh_3Cl)_2(\mu\text{-}rac\text{-bnpsel-O,O})]$, with bnpsel = 1,2-bis(*n*-propylsulfinyl) ethylene;[100] $[SnPh_3Cl)_2(\mu\text{-}meso\text{-bpse-O,O})]$.[101]

Group 15: $[BiCl_3(dmso\text{-}O)_3]$,[102] $[BiBr_3(dmso\text{-}O)_3]$, $[BiI_2(dmso\text{-}O)_2(\mu\text{-}I)_2\text{-}BiI_2(dmso\text{-}O)_2]$, $[Bi(dmso\text{-}O)_8][Bi_2I_9]$;[103] $[BiX_3(phen)(dmso\text{-}O)_2] \cdot dmso$, with X = Cl, Br; $[BiI_2(phen)(dmso\text{-}O)_3][BiI_4(phen)]$, with phen = 1,10-phenanthroline; $[BiI_3(bipyridine)(dmso\text{-}O)]$.[104]

Average dimensions for metal sulfoxide complexes whose data have been updated with respect to the previous survey[4] are listed in Tables VIII and IX.

Bonding Modes

The present X-ray structural data confirm the preference of the platinum metals for sulfoxide S-bonding, unless strong π acceptor ligands are present, as in the case of ruthenium. All harder metal ions generally form O-bonded complexes. It seems likely that the S-bonding present in the chelated tetracarbonyl chromium complex containing a sulfinylcarbene ligand[40] is due to the fact that chelation through oxygen would yield a strained six-membered ring.

A particular bonding mode is shown by the rhodium(I) complex with tetramethylthiophene S-oxide.[85] Because of π delocalization over the five-membered ring,[44] the metal, already π bonded to a cyclopentadienyl ring, prefers π bonding to thiophene instead of σ S-bonding to the sulfinyl group.

It is interesting to note that while ethane and ethylene disulfoxides act as S,S-chelating ligands with palladium,[53] platinum[92,93,105] and ruthenium,[30] with the tin hard acid, Ph_3SnCl, they act as bis-monodentate O ligands forming dinuclear complexes.[99,101] Interestingly, in the platinum dimer, $[\{cis\text{-}PtCl_2(PEt_3)\}_2(\mu\text{-}meso\text{-bpse-S,S})]$, the disulfoxide acts as a S-bridging ligand, with P and S atoms in *cis* positions, in order to avoid their competition for the metal d orbitals.[94] This unfavourable arrangement should have been reached in the case of formation of mononuclear S,S-chelated compounds.

Ethane disulfoxides have been assumed to form O-bonded chelates with the first series transition metals, on the basis of elemental analysis and IR spectroscopy.[106] However, the crystal structure determination of a copper complex, $[Cu\{rac\text{-}1,3\text{-bis}(n\text{-propylsulfinyl})propane\}_2](ClO_4)_2$, has shown that the ligand does not display chelating properties, but acts as a bis-monodentate ligand bridging the metal atoms to form layers of distorted square

TABLE VIII

Average dimensions for O-bonded metal sulfoxide complexes ($\langle x \rangle_s$ /Å, deg) with $\sigma(\langle x \rangle_s)$ in parentheses, together with σ and the number of averaged values in square brackets

M	M–O	M–O–S	S–O
Na(I) [a]	2.31(2) 0.05 [4]	131(11) 20 [3]	1.52(2) 0.02 [2]
Y(III) [b]	2.36(1)	131.3(7)	1.53(2)
Ln(III) [c]	2.37(1) 0.07 [23]	143(3) 11 [20]	1.512(1) 0.009 [23]
U(VI)	2.377(8) 0.024 [9]	131(3) 8 [9]	1.529(4) 0.013 [9]
Ti(IV)	2.11(1) 0.06 [17]	122.6(9) 3.6 [16]	1.527(3) [d] 0.010 [16]
Zr(IV)	2.202(5) 0.013 [7]	127.3(6) 1.6 [6]	1.539(1) 0.005 [7]
Cr(III)	1.981(7) 0.017 [5]	127.4(5) 1.2 [5]	1.538(6) 0.015 [5]
Mn(II)	2.162(9) 0.023 [6]	130(4) 10 [6]	1.505(3) 0.008 [6]
Ru(II)	2.126(6) 0.025 [16]	122.5(9) 3.5 [16]	1.538(3) 0.012 [16]
Os(III)	2.08(4) 0.06 [2]	123.55(5) [d] 0.07 [2]	1.54(3) 0.04 [2]
Ni(II)	2.15(5) 0.09 [3]	123(1) 2 [2]	1.518(4) 0.007 [3]
Cu(II)	2.03(3) 0.15 [34]	122(1) 7 [29]	1.523(4) 0.024 [31]
Hg(II)	2.46(8) 0.24 [9]	122(2) 6 [9]	1.527(6) 0.017 [8]
Al(III)	1.86(1) 0.02 [2]	122(8) 11 [2]	1.550(2) [d] 0.004
Sn(IV)	2.30(3) 0.16 [23]	126(1) 6 [24]	1.531(4) 0.021 [24]
Bi(III)	2.48(1) 0.04 [11]	126(1) 4 [13]	1.528(4) 0.007 [3]

[a] η^1 bonding. [b] One value only. [c] Ln = La, Ce, Nd, Eu, and Er. [d] $\langle x \rangle_u$.

TABLE IX

Average dimensions for S-bonded metal sulfoxide complexes ($\langle x \rangle_s$ /Å, deg) with $\sigma(\langle x \rangle_s)$ in parentheses, together with σ and the number of averaged values in square brackets

M	M–S	M–S–O	M–S–C	S–O
Ru(II) [a]	2.265(3) 0.025 [99]	117.7(2) 2.0 [92]	113.0(2) 2.4 [187]	1.478(1) [d] 0.010 [85]
Os(II) [a]	2.343(4) 0.007 [3]	114.3(7) 1.1 [3]	114(2) 3.2 [4]	1.479(8) 0.015 [3]
Pd(II) [a]	2.228(7) 0.022 [11]	115.7(6) 1.9 [9]	109.9(7) 3.1 [18]	1.466(5) 0.016 [10]
Pt(II) [a]	2.217(2) 0.026 [126]	116.3(2) 1.9 [124]	110.7(2) 2.6 [233]	1.467(1) 0.013 [98]
Pt(II) [b]	2.275(9) 0.018 [4]	118(1) 2 [4]	110(1) 3 [8]	1.475(3) 0.005 [4]
Pt(IV) [a,c]	2.301(2)	112.9(3)	109.9(3)	1.449(6)

[a] Not *trans* S. [b] *Trans* S. [c] One value. [d] $\langle x \rangle_u$.

planar CuO_4 groups.[107] O^O chelation seems unlikely for the formation of seven-membered rings. Analogously, in the case of the ruthenium(II) disulfoxide complexes, S^O chelation does not happen, probably to avoid formation of unstable six-membered rings. In fact, a MM stereochemical investigation on [$RuCl_2$(1,2-bis(methylsulfinyl)ethane$)_2$] has shown that the most stable isomers correspond to S^S chelates, with formation of five-membered rings whose strain energies depend on the chirality of the sulfur atoms.[108] It is worth noting that when *rac*-bpse reacts at 70 °C with triphenyltin chloride to form the 1:2 adduct, the coordinated ligand is found in the *meso* form, showing that configurational inversion occurred for one sulfur atom,[101] in contrast to the usual inertness of these ligands. Bridging ability is also displayed by cyclic disulfoxides, such as *trans*-1,4-dithiane-1,4-dioxide, which have been found to form solid state polymers with several lanthanide(III) ions.[71,72]

It is known that monosulfoxides can form different types of bridges depending on the nature of the connected atoms. Thus, a μ_2-S,O bridging type is usually found in ruthenium or platinum S-bonded sulfoxide complexes interacting with alkaline metal ions,[4] while the μ_2-O,O type is found in alkaline metal ion complexes, such as the sodium dimer [Na($OC_6H_3Bu^t$-2,6)-(μ_2-dmso-O)(dmso-O)]$_2$,[69] where each dmso ligand bridges two sodium ions through its oxygen atom. In the dinuclear Ru-Li complex, [Ru_2Br_6(tmso-S)$_6$-Li_2(tmso-O)$_2$(μ_2-tmso-O)$_2$(μ_3-tmso-S,O)$_2$], besides the η^1-S and η^1-O tmso li-

gands, there are μ_2-O,O and μ_3-S,O,O bridges that connect, respectively, two alkaline metal ions (*via* O), and one Ru (*via* S) and two Li ions (*via* O).[109] Only very recently, the unusual μ_2-S,S bridges between ruthenium atoms have been found, in $[Ru_2Cl_2(dmso\text{-}S)_3(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}dmso\text{-}S,O)]$[80] and $[Ru_2Cl_4(CO)_2(dmso\text{-}S)_3(\mu\text{-}Cl)(\mu\text{-}dmso\text{-}S,O)]$.[81] It seems likely that this kind of bonding can be present only in complexes having either a metal–metal bond supported by other bridging ligands,[80] or strong π acceptor ligands which 'harden' the metal centre, favouring the O-bonding.[81]

Updated average values for O- and S-metal coordinated sulfoxides are reported in Tables X and XI, respectively, confirming that upon O-coordination a significant lengthening (0.036 Å) of the S–O bond distance is observed with respect to free sulfoxides, while it is shortened (0.019 Å) upon S-coordination.

Inspection of Tables VI, VII and X, XI shows that the semi-weighted ($<x>_s$) and unweighted ($<x>_u$) means are virtually identical, as are their standard errors, showing that environmental effects, like those deriving from crystal packing, are very important.[110] The error of the weighted mean ($<x>_w$), as already observed,[110] is exceedingly low. The largest deviation from a normal distribution is found for the M–O–S bonds including all available

TABLE X

Average bond lengths /Å and angles /° in O-bonded metal sulfoxide complexes

	S–O	S–C	M–O–S	M–O–S [a]	C–S–C	O–S–C
min.	1.470	1.540	111.3	112.0	86.0	97.0
max.	1.578	1.915	161.3	130.0	122.0	115.9
n	249	344	267	205	238	509
σ	0.018	0.027	8.5	3.7	2.3	1.9
median	1.527	1.780	123.6	122.2	98.9	104.2
q_l	1.517	1.770	120.6	119.6	98.0	103.2
q_u	1.540	1.790	128.6	124.6	99.8	105.4
% ($\pm 2\sigma$)[b]	94.3 (0)	95.6 (3)	93.9 (3)	94.1 (0)	97.5 (2)	96.5 (3)
$<x>_s$	1.528	1.780	125.7	122.3	98.9	104.34
$\sigma(<x>_s)$	0.001	0.001	0.5	0.3	0.1	0.08
$<x>_u$	1.527	1.780	125.7	122.2	98.9	104.35
$\sigma(<x>_u)$	0.001	0.001	0.5	0.3	0.1	0.08
$<x>_w$	1.5289	1.7795	125.81	122.89	98.98	104.07
$\sigma(<x>_w)$	0.0004	0.0004	0.02	0.02	0.03	0.02

[a] Excluding values >130°. [b] No. of outliers (4σ) in parentheses.

TABLE XI

Average bond lengths /Å and angles /° in S-bonded metal sulfoxide complexes

	S–O	S–C	M–S–O	M–S–C	C–S–C	O–S–C
min.	1.422	1.717	109.4	100.4	89.3	99.5
max.	1.512	1.911	129.5	120.3	112.1	114.8
n	302	486	342	650	310	648
σ	0.013	0.019	2.5	2.9	2.3	1.7
median	1.471	1.781	116.9	111.9	100.1	107.3
q_l	1.463	1.773	115.3	110.0	99.0	106.3
q_u	1.480	1.792	118.5	113.5	101.7	108.6
% ($\pm 2\sigma$)[a]	94.0 (0)	96.9 (3)	96.2 (1)	94.2 (0)	95.2 (2)	95.2 (3)
$\langle x \rangle_s$	1.4731	1.7844	116.9	111.7	100.3	107.34
$\sigma(\langle x \rangle_s)$	0.0006	0.0008	0.1	0.1	0.1	0.07
$\langle x \rangle_u$	1.4719	1.7843	117.0	111.7	100.3	107.40
$\sigma(\langle x \rangle_u)$	0.0008	0.0009	0.1	0.1	0.1	0.07
$\langle x \rangle_w$	1.4764	1.7845	116.93	112.50	100.58	106.86
$\sigma(\langle x \rangle_w)$	0.0003	0.0003	0.01	0.01	0.02	0.01

[a] No. of outliers (4σ) in parentheses.

data (Table X), whose distribution is also characterized by a very large standard error σ (8.5°). In fact, very wide angles are found for lanthanide (range, 125.6–161.3°) and uranium (range, 124–149°) complexes, because of the ligand overcrowding due to the high metal coordination numbers. Wide angles can be also found in sodium complexes, as well as in a few cases of Mn(II), Ru(II), Cu(II) and Sn(IV) derivatives, for particular bonding situations. Excluding all these angles greater than 130°, a *quasi* normal distribution is obtained with an average M–O–S angle of 122.3(3)° and σ = 3.7°.

It is interesting to note that H-bonding causes a slight but significant lengthening of the S–O bond distance also in S-bonded metal sulfoxide complexes, as shown in the three hydroxylamonium salts of [*fac*-$RuCl_3$-(dmso-S)$_3$] reported above,[77] and in [*fac*-$RuCl_3$(dmso-S)$_2$(N_2H_5)].[78] In fact, the S–O bond length passes in the four compounds from 1.478(2) Å, in the absence of H-bonding, to 1.492(2) Å, in the presence of strong H-bonds.[77,78]

A similar lengthening has been also observed when S-coordinated sulfoxides interact electrostatically, through the O atoms, with alkaline metal ions [S–O, 1.487(2)–1.495(6) Å],[4] becoming much more marked in the case of covalent interactions, like in the case of the $Ru_2(\mu_2$-dmso-S,O) complexes, where the S–O distances are of 1.508(5) and 1.532(4) Å.[80,81]

The pretty large set of data collected clearly shows the tendency of sulfoxides, both in free and coordinated forms, to interact with hydrogen and alkaline metal ions. The strength of the interactions is revealed by the lengthening of the S–O bond distances.

The diiodo and the chloromethyl platinum(II) complexes, [*trans*-PtI_2-(dmso-$S)_2$][89] and [*trans*-PtClMe(dmso-$S)_2$],[90] represent together with [*trans*-$PtCl_2$(dnpso-$S)_2$] (dnpso = di-*n*-propyl sulfoxide),[111] to the author's best knowledge, the only examples of isolated platinum compounds containing *trans* dmso ligands, whose X-ray structure has been determined, in contrast with the large amount of data available for *cis* compounds.[4] In fact, the *trans* geometry is thermodynamically unstable and the complexes readily isomerize to the *cis* derivatives.[90,111] Apparently, iodine is bulky enough to destabilize its *cis* arrangement, favouring the *trans* geometry of the sulfoxide ligands. In fact, *trans* compounds have been isolated only in the case of very sterically demanding sulfoxides, like di-*n*-propyl, methylbenzyl or diisoamyl derivatives.[111] On the other hand, electronic factors are also important, like in [*trans*-PtClMe(dmso-$S)_2$], where the geometry is probably determined by the strong σ *trans* influence of the methyl group, which prevents formation of a *trans* C-Pt-S system.[90]

The Pt-S bond length of 2.289(2) Å in [*trans*-PtI_2(dmso-$S)_2$] is very close to that of 2.292(2) Å in [*trans*-$PtCl_2$(dnpso-$S)_2$], while it is longer than the mean value of 2.259(2) Å found in [*trans*-PtClMe(dmso-$S)_2$]. Unfortunately, lack of structural data does not allow a discussion of the role of the different ligand electronic and steric factors. However, all these distances are significantly longer than the average value of 2.217(2) Å found in *cis*-Pt(II) sulfoxide complexes, supporting the mutual *trans* influence effects of sulfoxide ligands.

The stereochemical and conformational features of ruthenium(II)[25] and ruthenium(III)[111] sulfoxide complexes have been rationalized through MM calculations after derivation of specific force-field constants. The analysis of possible isomers of [*mer*-$RuCl_3$(dmso)$_3$] and [*mer*-$RuCl_3$(dpso)$_3$] has shown that the isomer stability is essentially determined, through enthalpic and entropic contributions, by the bulkiness of the sulfoxide ligand, as measured by its cone-angle, *Θ*. Thus, for dmso (*Θ* = 99.6°), the most stable isomer is [*mer,cis*-$RuCl_3$(dmso-$S)_2$(dmso-O)], while for dpso (*Θ* = 106.7°) it is [*mer,cis*-$RuCl_3$(dpso-$O)_2$(dpso-S)].[112]

Conformational Features

As regards the possible rotation about the S–O bond in dmso-O complexes, strain energy calculations have shown that the most frequently found (≈70%) *trans-trans* geometry [4] corresponds to a minimum in the strain en-

ergy profile, as calculated for [*cis*-$RuCl_2$(dmso-S)$_3$(dmso-O)], while the less frequent *cis-cis*, *cis-trans* and *trans-cis* geometries (≈ 10% each) correspond to higher strain energy minima.[25] Finally, as regards rotation about the coordination bonds, it has been shown that rotation about the Ru–O bond is less hindered than that about the Ru–S bond, so that O-bonding should be favoured by conformational entropy contributions.[25] The self-consistent force-field developed for Ru(II) complexes has been also used to investigate the rotamer distributions of compounds containing lopsided nitrogen ligands, determined by hindered rotation about the Ru–N σ bonds. A satisfactory agreement with experimental NMR results in solution has been obtained.[25–27]

A conformational analysis of the [*fac*-$RuCl_3$(dmso-S)$_3$]$^-$ anion has shown that, in the minimum energy structure, the three dmso ligands are oriented in such a way as to have the three oxygen atoms at the vertices of an equilateral triangle (O···O, 3.270 Å), so that their plane is parallel to the plane defined by the three sulfur atoms (dihedral angle $\alpha = 0°$), and as far as possible from the chloride plane.[77] Higher energy rotamers are characterized by different O···O distances and a skewed arrangement of the O and S planes ($\alpha \approx 22°$). Inspection of the dmso arrangement observed in complexes containing the [*fac*-RuX_3(dmso-S)$_3$] group (X = Cl, Br) shows that it is very close, independently of intermolecular interactions, to that of the mimimum energy structure calculated for the isolated anion, showing that it is strongly determined by intramolecular interactions.[77] Substitution of X ligands with other groups, such as O-bonded dmso or nitrogen bases, changes the inter-ligand interactions modifying the orientation of the three *fac* dmso ligands in the minimum energy structure. For example, for [*cis*,*fac*-$RuCl_2$-(dmso-S)$_3$(dmso-O)] the minimum energy structure corresponds to $\alpha = 25.8°$, while the conformer with $\alpha = 2.7°$ has an energy 5.4 kJ mol^{-1} higher.[113] Interestingly, three polymorphs (F1–F3) of this complex have been isolated so far, and polymorph F3 ($\alpha = 24.2°$) is thermodynamically more stable than F1 ($\alpha = 2.3°$) and F2 ($\alpha = 0.8°$), in agreement with the trend of the molecular strain energies.

The influence of the ancillary ligands on the mutual sulfoxide geometry is further shown by the results of a conformational study on the rhodium and iridium (M) complexes [(η^5-C_5Me_5) *fac*-M(dmso-S)$_3$]$^{2+}$.[114] Here, substitution of X_3 with (η^5-C_5Me_5) causes a completely different arrangement of the sulfoxide ligands, because of the quite different intraligand van der Waals and electrostatic interactions.

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SAŽETAK

Stereokemijske značajke sulfoksida i njihovih kompleksa s metalima

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Daje se pregled najnovijih geometrijskih parametara nekoordiniranih sulfoksida i njihovih kompleksa s metalima, odakle se izvode prosječne vrijednosti duljina valentnih veza i veznih kutova. Prosječna duljina veze sumpor–kisik za nekoordinirane sulfokside iznosi 1,4918(9) Å. Nakon koordiniranja sulfoksida preko kisikova atoma na atom metala spomenuta se veza produlji do 1,528(1) Å, ali se u slučaju koordinacije liganda ostvarene preko sumpora ona skrati do 1,4731(6) Å. Vezivanje sulfoksida i mogućnosti premošćivanja razmatrane su zajedno s nekim njihovim stereokemijskim značajkama.